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THE SIGNIFICANCE OF CHANGING ATOMIC VOLUME.

III. — *THE RELATION OF CHANGING HEAT CAPACITY TO CHANGE OF FREE ENERGY, HEAT OF REACTION, CHANGE OF VOLUME, AND CHEMICAL AFFINITY.*

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I. Systems Involving a Minimum of Concentration Effect.

Julius Robert Mayer showed, sixty years ago, that when a gas is compressed, the work of compression reappears almost exactly as heat. One of the circumstances which permitted the discovery of this relationship is the fact that the heat capacity of a gas at constant volume is approximately independent of the volume. If the heat capacity of the gas were diminished by the compression while the other influences remained unchanged, it is clear that some of the heat energy already in the system would be displaced by the compression, and hence that the apparent evolution of heat would be made up of two added quantities, one due to the work put into the system from the outside, and the other due to the lessened heat capacity of the system. Thus the total evolution of heat would be greater than the heat corresponding to the work which had been done upon the system, unless the diminution of heat capacity involved the storing of energy in potential change. In order to develop the reasoning, step by step, this latter possibility will be waived for the present, and taken up again after the facts have been studied.

If $\mathfrak{U}$ is used to represent the unknown total heat energy necessary to raise the original system from the absolute zero to the reaction temperatures, $\mathfrak{U}'$ that necessary to raise the final system through the same interval, W the outside work done upon the system, and U the heat actually evolved, we may represent the possible relationship as follows: —

$$U = W + \mathfrak{U} - \mathfrak{U}'$$

Unfortunately $\mathfrak{U}$ and $\mathfrak{U}'$ are not definitely known, hence the exact solution of the equation is not possible at present. Nevertheless, a qualitative study of the situation in the light of the facts leads to inter-

esting results, as will be shown. In the case of a perfect gas $\mathfrak{U} = \mathfrak{U}'$, hence the above equation reduces to the form $U = W$, the fact pointed out by Mayer. $\mathfrak{U}$ and $\mathfrak{U}'$ are of course functions of the respective heat capacities.

The analogy which has been shown to exist between the work of chemical compression and the work of gaseous compression * seems to afford a means of extending this logic to the liquid and the solid condition, and thus to afford a clue to the vexed question as to the relationship of free energy and total energy.

It is well known that the heat capacity of a solid or liquid system usually changes slightly during the course of a reaction, and it has been shown in numerous isolated instances that compression usually tends to diminish the heat capacity of solids and liquids. † The diminishing specific heat with increasing specific gravity of the allotropic forms of sulphur, phosphorus, silicon, and carbon may be mentioned as other examples of the same general principle.

We should expect, then, if no other complications are involved, to find an excess of heat evolved, over and above the chemical work concerned in the reaction, in all those cases where the heat capacity diminishes during the reaction, and vice versa. But what measures have we of the chemical work involved?

By many the "free energy," or the energy available for *outside* work, is taken to represent the chemical energy. ‡ For the sake of argument, let us assume temporarily that this is the case, always bearing in mind

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* After the preceding paper was printed, my attention was kindly called to the fact that in 1881 Müller-Erzbach pointed out the parallelism of contraction and heat of reaction in some cases (Ber. d. d. ch. Ges., **14**, 217, 2043; Wied. Ann., **13**, 522.) More recently, Hagemann has called attention to the same relation (a brief paper published privately by Friedländer of Berlin in 1900). These facts were wholly unknown to me at the time of writing. The reason why the discovery has not had more effect upon chemistry is undoubtedly because these investigators did not call attention to the effect of the different compressibility of different substances, and drew no corresponding conclusions from the observations. Unless compressibility is considered, the exceptions to the rule are too frequent to permit satisfactory generalization. For examples of the express or implied denial of the significance of this relation, see Ostwald, Grundriss der allgem. Chem., 187 (1899), also Békétoff, Chem. Centralblatt 1894, II. 229. In neither case was compressibility considered.

† Richards, These Proceedings, **37**, 399 (1902); Regnault, Ann. Chim., **73**, 15 (1840); Thomsen, Thermo-chem. Untersuch., **1**, 52 (1882); Kahlbaum, Zeitschr. anorg. Chem., **29**, 177 (1902).

‡ Ostwald, The Chemometer, Zeitschr. phys. Chem., **15**, 399 (1894).

the fact that it is an assumption, and being ready to abandon the position when it has been proved untenable.

The immediate problem under investigation then resolves itself into the following question: Has the change of heat capacity any definite causal relationship to the relative magnitudes of the free-energy change and the heat of the reaction?

Throughout this paper the inductive method rather than the deductive one is to be used in all the reasoning. Hence the first step is the comparison of actual data concerning a number of carefully studied reactions.

Unfortunately the change in free energy can be computed from actual data only in the case of easily reversible changes; and these form but a small minority of the cases of chemical reaction. The reversible galvanic cell was shown by Helmholtz * to belong to this class, and may therefore be used as an example.

Among the many galvanic cells which have been measured, not all are immediately available for the present purpose. In the first place, only a few heat capacities of solutions have been accurately determined; and in the next place, in some of the cells perceptible electromotive energy is to be ascribed to the unequal balancing of osmotic pressures, which has nothing to do with the affinities involved. We must then select cells containing two liquids in which the extent of ionization and the migration velocities are similar, the anion identical, and the electromotive force and heat of reaction well known. The series of reversible cells which seems to fulfil these conditions most satisfactorily is that composed of pairs of the sulphates of copper, nickel, iron, zinc, and magnesium. The heat capacities of these solutions have been accurately determined by Marignac † and Thomsen ‡ and the electrical potentials have been determined by Wright and Thompson. §

In order to illustrate more clearly the table containing the results obtained from these cells, a single case may be given here in detail. The common Daniell cell is chosen for this purpose, using solutions of the strength $MSO_4 . 200H_2O$ because the heat capacities of such solutions

* Helmholtz, Sitz. ber. Berlin Acad., 2 February and 7 July (1882), Ges. Abh. Bd. II.

† Marignac, Ann. Chim. (5), **8**, 410 (1876).

‡ Thomsen, Pogg. Ann., **142**, 337 (1871).

§ Wright and Thompson, Phil. Mag. (5), **17**, 288 (1884), **19**, 1 (1885). This work is revised in connection with others by Wilsmore, Zeitschr. phys. Chem., **35**, 291 (1900).

have in every case been carefully determined. The chemical reaction taking place in the cell may be represented by the following equation: —

$$Zn + CuSO_4 \cdot 200H_2O = ZnSO_4 \cdot 200H_2O + Cu.$$

The change in the heat capacity of this system may be computed easily by subtracting the total heat capacity of the factors from that of the products. The "absolute" standard of heat capacity, the *mayer* * (or the heat capacity which is raised 1° C by 1 joule of energy), is peculiarly convenient for calculations of this kind; hence it is used below. The following table contains the data in question: —

Factors.	mayers.	Products.	mayers.
$CuSO_4\ 200H_2O$		$ZnSO_4\ 200H_2O$	
$(0.9516) \times (3762.7) \times (4.181)$	= 14,970	$(0.9523) \times (3764.5) \times (4.181)$	= 14,989
Zn	= 26	Cu	= 24
Total Factors	14,996	Total products	15,013
		Difference	17

Thus the heat capacity of the system is increased by 0.11 per cent during the reaction.

Since this is the case, we should expect to find that some of the heat energy actually evolved in the reaction would be needed to "fill" the extra capacity, and hence would not become manifest as rise of temperature. As a matter of fact, the observed evolution of heat energy in the reaction (210 kilojoules) is less than the electromotive energy ($1.10 \times 96{,}580 \times 2 = 213$ kilojoules) by about 3 kilojoules. Hence the data are consistent with the theory as to sign; and since both figures are small in proportion to the totals, the order of magnitude might also be consistent.

A single case does of course suffice to prove a point of such importance, hence ten galvanic cells, comprising every combination of the five metals before mentioned, are given in the following table.

Wright and Thompson used amalgamated zinc, but Richards and Lewis † have shown that amalgamation makes no essential difference in the potential of this metal, because of a singular compensation of effects. The table explains itself; the fourth and eighth columns contain the significant results to be compared, namely the change in heat capacity and the so-called "bound energy."

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* Richards, These Proceedings, **36**, 327 (1900).

† Richards and Lewis, Zeitsch. phys. Chem., **28**, 1 (1899).

Factors in Reaction.	Heat Capacities of MSO_4+200H_2O+M'.		Loss of Heat Capacity during Reaction.	Electromotive Force.	Electromotive Energy.	Observed Heat of Chemical Reaction.	"Bound Energy," or Excess of Heat evolved over Electromotive Energy.
	Factors.	Products.					
	mayers.	mayers.	mayers.	volts.	kiloj'les.	kiloj'les.	kilojoules.
$Ni+CuSO_4$	14,997	14,966	+ 31	0.57	111	131	+ 20
$Fe+CuSO_4$	14,996	14,955	+ 41	0.69	134	156	+ 22
$Zn+CuSO_4$	14,996	15,013	− 17	1.10	213	210	− 3
$Mg+CuSO_4$	14,995	14,889	+106	1.81	350	530	+180
$Fe+NiSO_4$	14,967	14,957	+ 10	0.12	23	24	+ 1
$Zn+NiSO_4$	14,966	15,016	− 50	0.53	103	81	− 22
$Mg+NiSO_4$	14,966	14,891	+ 75	1.24	240	400	+160
$Zn+FeSO_4$	14,955	15,015	− 60	0.41	79	57	− 22
$Mg+FeSO_4$	14,955	14,890	+ 65	1.12	217	375	+158
$Mg+ZnSO_4$	15,014	14,890	+124	0.71	138	319	+181

The data in this table are reduced as nearly as possible to the same standards. The heat capacities and electromotive forces correspond to solutions containing two hundred molecules of water to every molecule of salt; the electromotive force scarcely changes with dilution. It is not always easy to ascertain from Thomsen's statements the dilution corresponding to the heat of reaction, but in every case the solutions were at least as dilute as this, being sometimes of twice the dilution. Here also such further dilution can cause but a negligible effect on the result. The atomic weights used in Thomsen's work were unusually crude, even for that day, and all his results have been recalculated to correspond to more accurate values. For example, the values given by him for magnesium correspond to the value 24. instead of 24.36; and accordingly since magnesium itself was weighed, all his data for this element must be raised by one and one-half per cent.* The details of these and other similar calculations may be omitted, since their outcome does not seriously affect the conclusions attained.

* In passing it may be pointed out that a complete recalculation of *all* heats of reaction would be demanded if the standard of atomic weights were changed to O = 15.879.

It will be observed that in every case the loss of heat capacity has the same sign as the excess of heat evolved; and in general, where one is large the other is also large. This relationship is illustrated by the accompanying diagram. In comparing differences between such large numbers one could hardly expect exact parallelism; but the two phenomena run so closely together that one is forced to infer the existence of a fundamental connection between them.

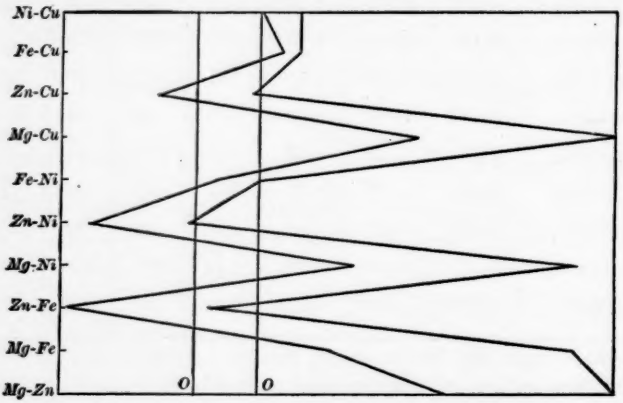


DIAGRAM ILLUSTRATING PARALLELISM OF CHANGE OF HEAT CAPACITY AND "BOUND ENERGY."

NOTE. The left-hand zigzag line depicts change of heat capacity in the ten cells given in the previous table, and the right-hand zigzag line depicts the "bound energy" or the difference between the heat of reaction and the available free energy of the reaction. In order to avoid confusion, these curves are referred to different ordinate axes, indicated by the two vertical zero lines.

A few more similar cells with other anions might have been added to this list from the data of Wright and Thompson, Marignac, and Julius Thomsen. The following exhibit relationships similar to those already given in detail: zinc-copper nitrate; zinc-lead nitrate; zinc-magnesium nitrate; lead-copper nitrate;* lead-magnesium nitrate; copper-magnesium nitrate; zinc-magnesium chloride. Unfortunately the great bulk

* The heat value for this cell, calculated from the results of Jahn (Wied. Ann., **17**, 593 [1882]), do not at all agree with the results of Thomsen. For the Ag-Cu-nitrate cell Jahn gives 10.6 Cal. per gram equivalent, while Thomsen gives 17.8 Cal.; and for the Ag-Pb-nitrate cell Jahn gives 21.5 Cal., while Thomsen gives 25.6 Cal. The value for the Pb-Cu-nitrate cell would then be 10.9 Cal. according to Jahn, and 7.8 according to Thomsen. I selected the latter value.

of the remaining data cannot be utilized at present because of a lack in each case of one or two of the necessary figures.

More complicated cells, in which also the osmotic tendencies are nearly balanced, show the same tendency. For example, in the cell Hg, HgCl, KCl, KNO_3, KBr, HgBr, Hg, which has been studied by Bugarszky,* there is a loss of heat capacity of about 26 mayers per gram equivalent during the reaction, while the observed heat energy exceeds the electromotive energy by 4.3 kilojoules. When the iodides are substituted for the bromides, the loss of heat capacity is 13 mayers, and the electromotive energy is less than the heat energy by 8.2 kilojoules. On the other hand, when mercurous oxide and potassic hydroxide are combined with the calomel electrode, a cooling reaction yields an electromotive energy algebraically 23.5 kilojoules greater than the heat energy, while the heat capacity gains 44 mayers. These figures are of the same order of magnitude as before, and in the expected direction. They are not included in the table because in them the osmotic energy may amount to an appreciable quantity, which cannot be wholly determined until the solubilities of the nearly insoluble salts are known.

Among all the cells which have been studied, including nearly if not quite all of those for which even moderately accurate data exist, only the cells containing aluminum as one of the metals disagree with the generalization. The solutions of salts of aluminum have usually a very large heat capacity, but yet the heat evolved is greater than the electromotive energy. Great discrepancies exist in the determination of this last quantity, however; for Wright and Thompson give as the potential of the cadmium-aluminum chloride cell only 0.05 volt †, while Neumann's ‡ values indicate 0.87 volt. It is not impossible that even the latter may be too low; for aluminum may be like chromium in its anomalous electrochemical behavior. § In the light of the discrepancy it seems permissible to reject the cells containing aluminum until more certain knowledge is obtained. From the accepted data two important connected inferences may be drawn with considerable security. In the first place, it appears that *unchanging heat capacity is an essential condition in determining the equality of the free electrical and the total heat energy changes, in reactions from*

* Bugarszky, Zeitschr. anorg. Chem., **14**, 145 (1897).

† Wright and Thompson, Phil. Mag. [4], **19**, 117 (1885).

‡ Neumann, Zeitschr. phys. Chem., **14**, 225 (1894).

§ The use of aluminum as a current rectifier is well known (Graetz, Wied. Ann., **62**, 189; Pollack, Zeitschr. phys. Chem., **24**, 546.). The same question is concerned in this phenomenon.

which osmotic work is eliminated by the balancing of nearly equal pressures. In the next place, as has been stated, the *sign and magnitude of the difference between the free and total energy changes is dependent upon the sign and magnitude of the change of the heat capacity of the system.*

These inferences are of very great interest, for according to the well-known equation of Helmholtz, $n \epsilon_0 \pi - U = n \epsilon T \frac{\partial \pi}{\partial T}$ *, we know that the temperature-coefficient of the free energy change is a simple function of the difference between the free and the total energy change. Moreover, the effect of the change of heat capacity of the system on the total energy change was pointed out long ago by Kirchhoff in the well-known equation $-\Delta K = \frac{\Delta U}{\Delta T}$, where Δ represents a finite change.

Hence we may draw the further inference: The *change of the available or free energy of a reaction with the temperature must have some fundamental connection with the change of the total energy with the temperature.*

This fundamental connection becomes manifest on comparing the actual values of $\frac{\partial U}{\partial T}$ with those of $\frac{\partial A}{\partial T}$, the former quantity being given according to the equation of Kirchhoff by the change in the heat capacities, and the latter being calculated from the difference between the total and free energy changes by the equation of Helmholtz.

The following table contains the comparison: —

Factors of Reaction.	$-\Delta K = \frac{\partial U}{\partial T}$.	$\frac{A - U}{T = 291^\circ} = \frac{\partial A}{\partial T}$.
	mayers.	mayers.
1. $Ni + CuSO_4$	+ 31	− 69
2. $Fe + CuSO_4$	+ 41	− 75
3. $Zn + CuSO_4$	− 17	+ 10
4. $Mg - CuSO_4$	+106	−620
5. $Fe + NiSO_4$	+ 10	− 3
6. $Zn + NiSO_4$	− 50	+ 75
7. $Mg + NiSO_4$	+ 75	−550
8. $Zn + FeSO_4$	− 60	+ 76
9. $Mg + FeSO_4$	+ 65	−540
10. $Mg + FeSO_4$	+124	−623

* In this equation n represents the number of equivalents, ϵ_0 represents 96,580 coulombs, π the potential, U the total heat of action, and T the absolute temperature.

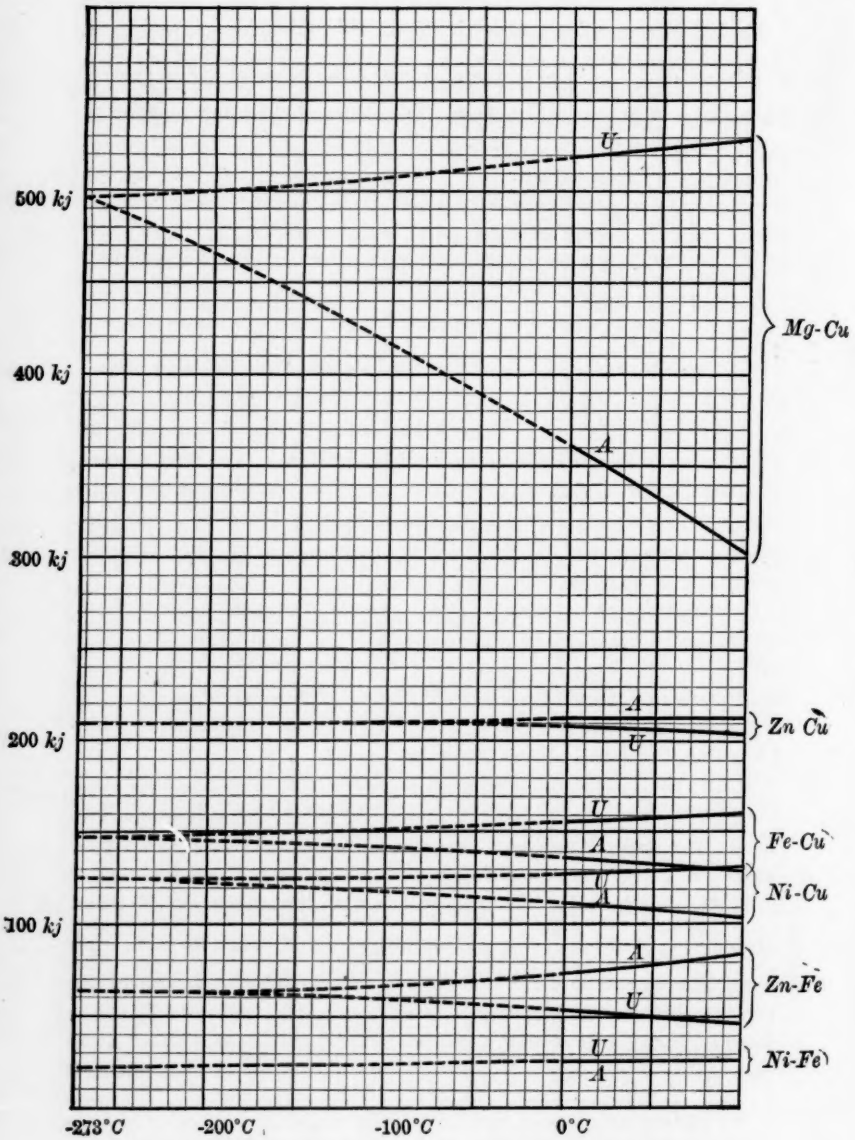
The last inference drawn above is supported by this table. Clearly $\frac{\partial U}{\partial T}$ is related to $\frac{\partial A}{\partial T}$. The two always bear opposite signs, and in general one is large when the other is large. The ratio of these two coefficients varies from 1 : 0.13 to 1 : 1.70, neglecting the fifth cell, where the values are too small to be significant. The average is 1 : 0.53 — that is to say, the free energy of a given reaction changes on the average about twice as fast as the total energy with change of temperature, but in the opposite direction. When the total energy increases, the free energy diminishes. Expressed algebraically, $\frac{\partial A}{\partial T} = -M\frac{\partial U}{\partial T}$, in which the value of M averages about 2.

The relation of these two series of data is pointed out yet more clearly by means of the accompanying diagram, in which several of the cells are represented graphically. In this diagram energy is plotted vertically, and temperature in the direction of the axis of abscissae. The lines marked U give the actual quantities of heat evolved in the chemical reactions, the change with the temperature being calculated from Kirchhoff's equation, while the lines marked A give the actual magnitude of the electromotive energy per gram molecule. (See next page.)

On extrapolating the several lines, it is evident that each pair tends to converge at a point not far from absolute zero. There is no reason for surprise at this fact; indeed, such a result is a necessary consequence of the equation of Helmholtz, in which $A - U = 0$ when $T° = 0°$. The interest centres about the fact that the U always increases when A decreases with the temperature, and vice versa.

It will be noticed that in order to converge at the absolute zero these lines must be not exactly straight, but slightly curved, — at least the lines for the free energy must be. This is only natural; for if U steadily increases with the temperature when A is diminishing, $U - A$ will grow at a rate which is greater than that due to the change in A alone. Hence $\frac{U-A}{T} = -\frac{\partial A}{\partial T}$ also will increase as the temperature rises. $\frac{\partial A}{\partial T}$ could be constant, or $A : T$ a linear relationship only in the case of the constancy of U. As a matter of fact Bugarzsky's results enable one to conclude that the temperature coefficient is on the average about 3 per cent higher at 30° than it is at 10°.* Of course more accurate measure-

* This calculation is based upon all except one of the cells for which Bugarzsky gives data. The mercuric sulphide cell is rejected because of known irregularity. Zeitschr. anorg. Chem., **14**, 157 (1897).



U = heat of reaction. A = electrical energy.

Ordinates represent energy, abcissae temperature (Centigrade).

ments are necessary to attain a precise knowledge of this relationship of the temperature coefficients; and moreover it probably differs with different cells. The foregoing calculations are merely for the purpose of orientation.

Qualitatively all the results correspond with the theory at first proposed. In every case where the heat capacity diminishes, the heat evolved is greater than the free-energy change. But in some cases the difference is very great; and the suspicion arises that perhaps the free-energy change is at least as much smaller than the sum of the attracting energies as the heat of reaction is greater than this sum. Is there any method of determining quantitatively the heat which has been displaced by the change of heat capacity in order to test this question? If the free-energy change could be proved to be equal to the total-energy change after correction for change of heat capacity, it would be fairly safe to assume that this two-fold result really represented the attracting energies. If, on the other hand, the heat evolved is still the larger, even after correction for the change of heat capacity, there would be valid reason to suspect that the free-energy change is less than the sum of the affinities.

Thus the question is a very fundamental one; but unfortunately the exact computation of how much of the heat energy which has been needed to raise the system from the absolute zero is still present as heat vibration, and how much has been expended in separating the atoms, and thus stored as potential energy, is impossible.* Nevertheless, the heat still present as vibrational activity obviously cannot exceed the total heat which has been put into the system, and this total may be calculated with considerable exactness when the specific heat of ice at very low temperatures is known with accuracy.

For the present, as usual, an approximate calculation must suffice. Making allowance for every circumstance, it is hardly conceivable that more than 2500 kilojoules of heat energy have thus been introduced into the system $Mg + CuSO_4 + 200H_2O$, in order to raise it from absolute zero to 20°C. But in this system as given in the table on p. 297 the heat capacity changed 106 mayers during its subsequent reaction, or 0.71 per cent of the whole. This change, entirely apart from any heat which might be evolved from the affinities concerned, might cause an isothermal displacement of 0.71 per cent of the heat energy present,†

* Boltzmann has calculated that about half of the energy is used for each purpose, but the result is doubtful. Sitz. ber. Wien. Akad., **63**, II. 1871.

† This assumption is uncertain, but lack of data forbids greater accuracy (p. 293). The result given is probably a *maximum*, which is all that is desired.

or at most $0.0071 \times 2500 = 18$ kilojoules. The actual evolution of heat in excess of the free energy is, however, 170 kilojoules, a figure far greater than the calculated value. Other cells yield the same result; in no case in which osmotic phenomena cause no disturbance is the greatest possible amount of heat displaced enough to correspond to the deficiency of free energy. Two alternatives are now open, — either the free energy does not fully represent the "attracting energy," or else the heat evolved is too large to correspond to the "attracting energy," even after correction for the change of heat capacity.

Before going further it is well to define precisely one of the terms employed above. The phrase "attracting energy" is used to represent the sum of the work done by all those tendencies which exert a positive attraction. These tendencies may be three in number, — purely chemical attraction or "*chemism*" (such attraction as binds chlorine to itself in chlorine gas), *gravitation* (which seems to be important chiefly in the heavy metals), and *electrical attraction;* but if any other attractive tendencies exist, they too are included.

In the preliminary study of the phenomena of changing atomic volume, use was made of the possible analogy between an atom and an elastic sphere of gas, in which every portion of the interior gas was supposed to exert an attraction upon every portion of another similar sphere. Further use of this analogy makes it possible to explain the relation between free and total energy in a plausible manner. The illustration must, however, be somewhat modified as it becomes more detailed and concrete; for while the temperature of a sphere of gas is supposed to be traceable to the motion of molecules within it, we must imagine the temperature of an atom to be due to the elastic bodily oscillation of the greater part of its substance.

Two such elastic balls colliding in space would compress one another. Unless some adhesive tendency caused them to cling together, they would immediately fly apart again with their original velocities, tending to absorb as much heat in their consequent expansion as they gave out during compression. Except for the change of direction, their condition would be the same as if they had never met, and no violation of either the first or the second law of thermodynamics would be involved.

If, on the other hand, some attracting or adhesive tendency caused them to cling together, permanently and irreversibly, they would continue in internal oscillation, the additional energy * of which would be a

* That is to say, the energy over and above their original energy of progression before they affected one another.

direct measure of the energy of compression. But this additional oscillation would signify an evolution of heat.*

Suppose now that instead of colliding irreversibly, the two imaginary balls were arrested by an outside mechanism, being allowed to attain gently the same united equilibrium, thus utilizing the energy which would otherwise have become manifest in oscillations as outside work. It is conceivable that in this way all oscillation might be prevented, in which case no heat would have been evolved, and the equivalent of the energy which would otherwise have caused the oscillations will have been used for some outside purpose by the mechanism. The Daniell cell, or better, the Ni-Fe cell, may serve as the actual type of such a conception.

It does not necessarily follow, however, that the mechanism would be capable of using all the attracting energy, or would be able to perform an amount of outside work which would be equivalent to the heat. Indeed, the distortion of both atoms caused by their mutual compression might well be expected to cause an expenditure of energy within the atom; hence less would be available for outside work. Such distortion would naturally tend to restrict the heat vibration, and hence diminish the heat capacity. Hence one might have predicted that when there is a loss of heat capacity in the system, the free energy could not equal the attracting energy, and that some of the attracting energy must inevitably appear as heat, not available for outside work. In symbolic language, according to the first law of energy, $\mathfrak{C} = A' + \mathfrak{P}$, where $\mathfrak{C}$ represents chemical attracting energy, A' free energy, and $\mathfrak{P}$ energy needed to effect a diminution of heat capacity.

On the other hand, the vibrational activity of heat energy may be supposed to be continually striving to overcome the restrictions which circumstances impose upon it. Hence when the opportunity of an enlarged heat capacity is offered by the progress of a chemical change, this heat energy may be able to perform outside work in addition to

* A perfectly symmetrical elastic ball in collision with another symmetrical elastic ball might be supposed to cause this other to rebound reversibly even if attraction existed between them. As an illustration of this one may conceive of a perfectly elastic ball bouncing on a perfectly elastic surface under the influence of gravity, — its oscillation would continue forever. If, however, one or both of the atoms under consideration is irregular in shape, it is clear that the shock might be so split up into cross-vibrations as to scatter the energy which would otherwise have been used to cause the rebound. Thus heat would be evolved, and the union would be permanent. It is possible that this need of asymmetry in the atom may be the reason why simple pure substances will not combine, but need the catalytic effect of a third substance such as water.

that capable of being performed by the chemical affinity alone. The result would be a cooling reaction and an excess of free energy. This behavior would not be a contradiction of the second law of thermodynamics, because the law states only that heat cannot *of itself* do work at constant temperature.

Thus the hypothesis of compressible atoms not only is consistent with the ordinary applications of the two laws of energy, but also affords a conceivable picture of the cause of the newly discovered relation of $\frac{\partial U}{\partial T}$ to $\frac{dA}{dT}$.

On the basis of the present data it is unprofitable to attempt the calculation of the mathematical relation of $\frac{\partial U}{\partial T}$ to $\frac{\partial A}{\partial T}$, or to probe further into the mechanism of the change. When more exact data have been obtained, it may well be possible to arrive at more definite conclusions. If the contraction of volume on combination could only be interpreted in the light of accurate determination of the compressibilities involved, it seems reasonable that this contraction might be a more exact measure of the affinity than either the free or the total energy change.

The foregoing facts and logic seem to lead to the conclusion that the change of free energy of a process does not really represent the attractive energy at work in the process, unless the heat capacity of the system remains unchanged during the reaction. If the heat capacity diminishes during the reaction, the free energy is less than the affinity, and vice versa.

This conclusion is contrary to the common belief. If warranted, it shows that the free energy change is a no more satisfactory guide to the affinity than is the heat evolved in the reaction, even when no concentration effect is present. The free energy seems to represent rather the remainder left after a resisting energy has been subtracted from the attracting energy. Only when the heat capacity does not change during the reaction may we suppose that the attracting energy, the change of free energy, and the heat of reaction are equal. A consequence of this equality is that the attracting energy, like the free and total energy changes, cannot change with the temperature when the heat capacity is invariable.

It is of course true that the change of free energy is the total resultant effect which determines whether or not the reaction will take place. To put the question in another way, the present reasoning seems to afford

some basis for separating the change of free energy into two components, one representing the sum of all the attracting energies, and the other a resisting tendency which is connected with the restriction of the heat capacity. It seems to me that further light upon the question of atomic energy is to be had only by means of some such analysis of those composite effects which thermodynamics is content to leave superposed.

The results of this section may be summed up once more in the following sentences: —

When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and total-energy changes of the reaction are equal and unchangeable with the temperature, and each may be supposed to represent the total "attracting energy," — a term which covers gravitational and electrical attraction as well as purely chemical attraction.

When, on the other hand, in such a system the heat capacity of the system changes, it seems reasonable to suppose that the "attracting energy" lies between the free-energy and the total-energy change, one being too small and the other too large.

II. Systems involving Appreciable Concentration Effect.

Allusion has been made more than once to the osmotic or gas-pressure work which results from differences of concentration. Even in the most favorable cases given above, this modifying influence must have had a slight although negligible effect.

The present chapter will show how slight this effect may be supposed to have been, as well as indicate the manner of its action in other cases. It is well known, according to the work of Helmholtz, Nernst, and others, that in dilute solutions the potential due to difference of concentration is approximately represented by the equation $\pi = \frac{RT}{n\epsilon_0} \ln \frac{c_0}{c}$* if the reaction takes place in a constant volume and migration velocities are eliminated. When the solutions are so dilute that there is no heat of reaction, this equation represents quite closely the actual potential.

The effect of this osmotic work on the electrical potential of cells where heat-producing affinity is also at work is, according to the preceding analysis, best seen in those cells which exhibit no change of heat capacity under their operation. Such cells are those which involve simply the dilution of amalgams, which thus assume great theoretical

* c_0 = initial concentration, c = final concentration.

importance. Meyer * was the first to measure carefully cells of this type; but more accurate and significant measurements have been made since by Richards and Lewis † and by Cady ‡ under the direction of Bancroft.

The results of Cady are especially easy to interpret, because he worked with sodium amalgam, which has a large heat of dilution, even with fairly dilute solutions. He found that the electromotive energy of the cell Na 20.2 Hg — Na 86.7 Hg was equal to the sum of two quantities, the osmotic work and the heat of dilution. Expressed mathematically, $n\pi\epsilon_0 = RT \ln \frac{c_0}{c} + U$, where $\pi\epsilon_0$ is electrical energy, c_0 the concentration of the mercury in the stronger amalgam, c that in the weaker, and U the heat of dilution (135 cal. per gram atom). He showed that the electromotive force was independent of the nature of the solvent between the amalgams and the concentration of the dissolved electrolyte, and concerned the amalgams alone. U was shown to be constant between 4° and 22°.

This result is of the first importance, and taken in connection with the preceding considerations concerning the heat capacity, it seems to afford a new insight into the mechanism of electromotive energy. This energy must be looked upon as the sum of at least two quantities; in the first place of the free energy of the chemical reaction, which happens to be equal to the total energy in Cady's case because the heat capacities are unchanging, and in the second place of the osmotic energies at work. Only when the heat capacity is constant is the change of free energy of the chemical reaction equal to the total energy; hence in general Cady's result,

$$n\pi\epsilon_0 = RT \ln c_0/c + U,$$

is applicable only to such cases. When the heat capacity diminishes during the reaction the second member of the expression will be greater than the first, and vice versa. This possibility was not considered by Cady.

The outcome of all this inductive logic is essentially identical with the result attained deductively by Lewis. He found that from the first and second laws of thermodynamics and the gas law, with the help of a few assumptions, the following equation may be derived: —

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* Meyer, Zeitschr. phys. Chem., **7**, 477 (1891).

† Richards and Lewis, These Proceedings, **34**, 87 (1898); Zeitschr. phys. Chem., 28, 1 (1899).

‡ Cady, J., Phys. Chem., **2**, 551 (1898).

$$A = R\,T \ln \frac{c_0^{n_0} \cdots}{c^n \cdots} + U - T\int_{T_0}^{T} \frac{K_0 - K}{T}\,dT + H\,T.^*$$

In this equation there is only one unfamiliar symbol H, which signifies a sum of several integration constants. Since the last two terms are hard to determine practically in many cases, we may combine them and write

$$A = R\,T \ln \frac{c_0^{n_0} \cdots}{c^n \cdots} + U - f(K, T).$$

In words, the available energy of a reaction is equal to the sum of the concentration effect and the heat evolved, minus a quantity which is partially dependent upon change of heat capacity.

This is qualitatively the outcome of the reasoning based purely upon experiment. In one respect the experimental conclusion is more detailed than the theoretical, in that the former indicates the complete elimination of the last term where the heat capacity of the system does not change during the reaction, while the theoretical equation still contains an unknown constant of integration in this case.

A clearer insight into the matter is possibly to be obtained by writing this equation in the following form, in which $\mathfrak{C}$ represents the true although as yet unknown value of the attracting affinity, and $\mathfrak{P}$ is the work needed to change the heat capacity.

$$A = R\,T \ln \frac{c_0^{n_0} \cdots}{c^n \cdots} + \mathfrak{C} - \mathfrak{P}.$$

As Lewis has already pointed out from the deductive side, the equation of Nernst for the single potential difference of a reversible electrode should obviously be remodelled on the basis of these conclusions. The Nernst solution-pressure P must include not only the concentration effect, but also the effect of the free energy due to affinity of the solid electrode for the solution.†

The latter is really by far the most important part of the reaction. For the present purpose it is best not to include this effect in the vague and comprehensive P, but to separate the latter into its two important parts, thus

$$n\,\pi\,\epsilon = R\,T \ln \frac{P}{p} = R\,T \ln \frac{p'\,z}{p} = R\,T \ln \frac{p'}{p} + R\,T \ln z.$$

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* G. N. Lewis, These Proceedings, **35**, 1 (1899), Z. phys. Chem., **32**, 364.

† Lewis introduces also a term to cover the nature of the solvent in the cell. While this may be necessary, it seems probable that the value of A includes the effect of changing solvent.

In this equation p' indicates the true concentration effect or "thermal pressure" * of the pure metal, and z represents an imaginable pressure-effect of the affinity (called the "physicochemical potential" in a recent paper on driving energy †). The expression $RT\ln z$ indicates of course the outside work $\mathfrak{C} - \mathfrak{P}$ capable of being done by the affinity, and may be indicated by A' for the sake of brevity, according to the equation on p. 305. Then

$$n\pi\epsilon_0 = RT\ln\frac{p'}{p} + A'.$$

When the heat capacity is unchanging $\mathfrak{P} = 0$ and $A' = \mathfrak{C} = U$ and the equation reduces to the result found by Cady.

With the help of this equation it is possible to understand many relationships which would otherwise be inexplicable.

In solutions of equal ion-concentration, $RT\ln\frac{p'}{p}$ would be nearly the same for all metals. It is true that we are as yet uncertain concerning the true value to give p', for the so-called "mass-law" often does not apply to concentrated material; but a large change in p' would not cause a serious change in its logarithm. Considering the five metals already treated, if we assume the pressure to be inversely proportional to the volume, and suppose that a normal solution of the sulphate of each metal is about one quarter ionized (four liters containing about a gram-ion), the value of $RT\ln\frac{p'}{p}$ will range from $RT\ln\frac{4000}{6.7}$ in the case of nickel to $RT\ln\frac{4000}{13.3}$ in the case of magnesium. At 20° these values become $2.43 \ln 600 = 15.6$ kilojoules and $2.43 \ln 300 = 13.8$ kilojoules. Thus the range between the extremes is only 2 kilojoules, an amount not greater than a possible error in the heat of reaction in some cases. On the average, the concentration energy (or the pressure energy) of a metallic electrode in a normal solution of its sulphate is probably about 15 kilojoules per gram atom.

The only satisfactory actual data known to me concerning this concentration effect are those of Richards and Lewis ‡ published in the paper

* Lewis, These Proceedings, **36**, 145 (1900); Z. phys. Chem., **35**, 343.

† Richards, These Proceedings, **35**, 477 (1900). In this paper the relation between c and p is dwelt upon. It is by no means certain that anything is gained either in the present equation or in that of Nernst by assuming this chemical energy as a simple function of the temperature.

‡ Richards and Lewis, These Proceedings, **34**, 87 (1898); Z. phys. Chem. **28**, 1.

already quoted. In this work the electromotive force due to the concentration effect between zinc and a one per cent solution of zinc in mercury was found to be 0.0585, at 20° C; and of cadmium in the same way 0.0615. On diluting the amalgams to the concentration ratio of 400:1 to bring them into comparison with the calculation given above about 0.025 would be added to the electromotive forces, corresponding to a total of about 0.085 volt for this dilution. The electromotive energy is then $2 \times 96{,}580 \times 0.085 = 16.4$ kilojoules, or an amount quite close to the above values (14 to 15 kilojoules) calculated theoretically. More extended data of this kind would obviously be highly instructive; and it is our intention to study such cells experimentally in this laboratory in the near future.

Obviously then the electromotive energy of most reversible electrodes arise chiefly from the energy of the affinity, only about fifteen kilojoules per gram atom being probably due to the difference in concentration between the pure metal and ion. Since, moreover, this concentration effect cannot be very different with different metals, no great error will result if the appropriate multiple of this value is subtracted from each, in order to find the free energy due to the affinity proper. Evidently this procedure would leave the results on page 297 unchanged, since the same value would be subtracted from each electrode.

In the light of these facts, we should expect to find an approximate parallelism between electromotive force of a single metal in one of its salt solutions and the heat of ionization. Moreover, since the affinity of the metal for the water seems to be the cause of ionization, the heat of formation of the hydroxide and the contraction occurring during its formation should each exhibit a parallelism with each of these quantities. Of course considerable irregularities due as has been shown to changing heat capacity and varying compressibility would be expected, and all that can be done with the present data is to reduce the figures to comparable magnitude by adding or subtracting a constant from each series. This has been done in the following table. It is assumed that the heats of hydration of cupric, argentic, and mercuric oxides are zero.

It is clear that in general the expected parallelism actually exists. The deviations are not frequent enough to obliterate the meaning of the facts. This is especially so, since many of the deviations can be explained. The great compressibility of potassium and sodium and their comparatively expanded condition in the elementary state account for the relatively larger contraction to be observed in their cases. On the other

	Electromotive Force.	Electromotive Energy.	Heat of Ionization. (Ostwald).*	Heat of Formation of Hydroxide less 470 Kj.	Contraction if OH = 12 c.c.
	volts.	kilojoules.	kilojoules.	kilojoules.	cubic cent.
2 K	?	?	518	504	60.2
2 Na	?	?	480	468	33.8
Mg	1.49	288	456	439	12.2
⅔ Al	1.28 ?	253 ?	338	358	...
Mn	1.07	207	210	213	3.9
Zn	0.76	147	147	162	...
Cd	0.41	71	77	97	6.4
2 Tl	0.36	69	7	6	...
Fe	0.34	66	93	101	...
Co	0.23	44	71	81	5.0
Ni	0.23	44	67	70	...
Sn	0.16	31	14	101	...
Pb	0.15	29	2	26	...
2 H	0	0	0	102	...
⅔ Bi	−0.25	− 48	...	7	...
Cu	−0.34	− 66	− 66	− 28	− ?
Hg	−0.76	−150	− 83	− 97	− ?
2 Ag	−0.81	−156	−106	−159	− ?

hand, manganese is undoubtedly originally in a very compressed state, its large self-affinity being shown by its exceedingly high melting point; hence the contraction to be observed on forming the hydroxide is not as large as one would otherwise have expected.† Many other irregularities in the approximate parallelism of these four sets of data can be explained on the basis of the principles explained in the present paper and those preceding it, but until more exact figures are at hand, a closer comparison is not worth while.

* Grundriss, 281 (1899).

† Richards, These Proceedings, **37**, 11 (1901).

In this paper galvanic cells have been used as the most convenient means of measuring change of free energy, and therefore of testing the relation of this quantity to chemical affinity, change of total energy, heat capacity, and contraction of volume. It is clear, however, that all reactions, including such physical ones as vaporization, should indicate the same relationship.

As examples of the effects of changing heat capacity upon free energy, the familiar successes and failures of the law of Guldberg and Waage may be cited. In the most frequent case, when no outside work is done, the concentrations adjust themselves until their combined effect just balances the algebraic sum of the other sources of free energy.* The chief of these, the sum of the chemical affinities $\mathfrak{C}$ concerned, has already been discussed in a previous paper; but to this must be added the free-energy change concerned in change of heat capacity $\mathfrak{P}$. Since there is now no outside work, equation on page 309 becomes

$$0 = RT\ln\frac{c_0\cdots}{c\cdots} - (\mathfrak{C} - \mathfrak{P}),\dagger$$

or

$$RT\ln\frac{c_0\cdots}{c\cdots} = \mathfrak{C} - \mathfrak{P};$$

therefore

$$\ln\frac{c_0\cdots}{c\cdots} = \frac{\mathfrak{C} - \mathfrak{P}}{RT} = \text{“}k\text{.”}$$

Obviously this value will be constant only when the work concerned in the change of the heat capacity and the chemical affinity alter in the same way at the same time. In many cases this simultaneous change actually occurs, especially when the substances concerned are all similar, as in the case of the ester-formation, or the dilution of weak acids. The slight change in the heat capacity in these cases is not enough to cause a serious effect on the result.

The amount of the irregularity is often too small to be observed, but a single example may be given in order to show the real analogy to the case of the galvanic cells. It is well known, from the results of Berthelot and Saint Gilles and others, that the formation of ethyl acetate from equivalent amounts of alcohol and acetic acid is a reaction which attains equilibrium when two-thirds completed. That is to say, the tendency to run

* “The Driving Tendency of Physicochemical Reaction,” Richards, Journ. Phys. Chem., **4**, 385 (1900).

† In this case, since $\mathfrak{C} - \mathfrak{P}$ is working in the opposite direction from the other term, its sign will be minus.

in this direction is greater than the tendency to run backwards. The reaction is, however, a cooling one, absorbing perhaps 8 kilojoules per mole. The only available data concerning the heat capacity of the system indicate that there is, however, a considerable gain, perhaps 15 mayers, in this important quantity, as is usually the case when water is formed in a reaction. If it were not for this gain, the reaction would probably have been a warming reaction instead of a cooling one. Thus we have the anomaly of an exothermic reaction (exothermic in the sense that chemical energy is converted into heat) which causes a cooling effect, because the heat capacity is increased in yet greater measure.

With strong electrolytes, the deviations are more marked. Here dilution usually causes a continual decrease in heat capacity. But a decrease in heat capacity seems to involve the expenditure of available energy ($\mathfrak{P}$), therefore a diminution in $\mathfrak{C} - \mathfrak{P}$ and hence also in the "constant" equilibrium ratio $\ln \frac{c_0 \cdots}{c \cdots}$ balanced against it. That is, an increase in the volume causes an increase in the "constant" $\ln \frac{c \cdots}{c_0 \cdots}$. This corresponds qualitatively with the facts, for Rudolphi * found that upon multiplying the normal equilibrium ratio by a direct function of the volume ($\sqrt{v}$) a formula was obtained which represents the facts much more closely. Bancroft † has pointed out the variable nature of the exponent — a variation which would only be expected according to the present analysis.

In the light of these considerations, it is evident that neither "mass-law," vapor pressure, nor freezing point can give correct values for the extent of electrolytic dissociation; and since conductivity is affected by varying migration, it also is unreliable. Hence it would appear that each of the contestants in the recent unfortunately polemical discussion upon this subject is partly right and partly wrong. Nevertheless, although we have not yet data for determining the exact extent of dissociation, it seems to me a great mistake to reject wholly this useful and illuminating hypothesis.

Until more satisfactory data concerning heat capacity are obtained, it is idle to pursue this aspect of the question further, important as it seems to be.

On differentiating the equilibrium equation

$$\ln \frac{c_0^{n_0} \cdots}{c^n \cdots} = \frac{\mathfrak{C} - \mathfrak{P}}{RT}$$

* Rudolphi, Zeitschr. phys. Chem., **17**, 385 (1895).

† Bancroft, Ibid., **31**, 188 (1899).

the equation of van't Hoff is obtained only when $P = 0$, that is to say, when the heat capacity remains unchanged during the reaction. Evidently, therefore, the equation of van't Hoff, even in its differential form, represents an approximation of only the same order of accuracy as Berthelot's rule, and its deviations from exact fulfilment depend upon the same modifying circumstance. This fact also was inferred by Lewis in the paper already cited on theoretical grounds.

The study of the preceding data shows at once the reason why Berthelot's "rule of maximum work" holds in so many cases. Whenever the change of heat capacity is negligible, the total energy seems to express both the free energy and the attractive affinity. In most cases of simple reactions, the change of heat capacity is very small, and in such cases Berthelot's rule applies. Even in such an intense reaction as that of magnesium upon plumbic oxide the heat capacity changes by only about 6 mayers per gram molecule, which probably could not cause a difference of more than 10 kilojoules between the change of free energy due to affinity and the change of total energy, judging from the figures on page 297. This is a quantity so small in relation to the total heat of reaction (392 kilojoules) that it would not be noticed in an approximate comparison. When concentration effects come into play, in such simple reactions, it is evident that the heat of reaction expresses the affinity more nearly than the total free energy change, although of course it does not express the tendency of the reaction to take place.

The free energy of a reaction is that which can overcome outside obstacles, and hence can enable the change to occur. The heat of reaction seems to be due primarily to affinity, but its magnitude is modified by change of heat capacity. Hence a cooling reaction can occur from two causes: first, because of the loosening of affinities by an overpowering concentration effect working against those affinities, where A is positive in the expression, —

$$A = RT \ln \frac{{c_0}^{n_0}}{c^n} - A_1,$$

and secondly, because of a sudden increase in heat capacity during the reaction which causes a lowering of temperature without change in the quantity of heat present. These two effects often occur together, because the release from the compression caused by chemical union often involves gain of heat capacity. The former of these cooling causes is strictly endothermic in the sense that heat energy disappears, but the latter is not necessarily so, although it of course always tends to

produce a cooling effect. The latter form of reaction may be called "pseudo-endothermic."

Physical reactions involving change of state such as vaporization may be interpreted in a similar fashion. The extension of the argument would throw light upon Trouton's rule,* explaining the approximate regularity and the causes of the deviations, and would give a further insight into the relation between the liquid and the vapor states. For the present, however, this discussion must be postponed. In the near future these and many other aspects of the new kinetic conception will be considered in another paper.

III. Summary.

The conclusions attained in the following paper are summarized below. The first six are generalizations upon fact, the certainty of which is limited only by the moderate number of cases accessible. But one exception has been found, and the probable irreversibility of that reaction annuls its verdict. The last headings contain hypothetical inferences based upon the preceding considerations. It may be that the conclusions recorded below represent merely further approximations, to which exceptions may be found in the future; but the essential agreement of so many facts seems to indicate that at least they are steps in the right direction.

1. In a reaction from which concentration effects have been eliminated, where the total heat capacity remains constant during the reaction, the change of free energy and the heat evolved are equal.

2. When the heat capacity of such a system diminishes during a reaction, the heat evolved is greater than the change of free energy.

3. When the heat capacity of such a system increases during a reaction, the heat evolved is less than the change of free energy.

4. If in addition to these tendencies there is unbalanced osmotic or gas pressure, this pressure adds its share of work algebraically to the change of free energy treated in the three preceding paragraphs, according to the equations

$$A = RT\ln\frac{c_0^{n_0}\cdots}{c^n\cdots} + \mathfrak{C} - \mathfrak{P} = RT\ln\frac{c_0^{n_0}\cdots}{c^n\cdots} + U - f(\Delta K).$$

5. Thus in a complex cell containing precipitates the change of free energy, which represents the tendency of the reaction to take place, is by no means a measure of the attractive energy concerned, but has superposed upon this attraction at least two other modifying circumstances.

* Ostwald, Lehrbuch, I. 354 (1891).

6. The fact that in many reactions the change of heat capacity is small and the concentration effect about balanced affords an explanation for the frequent fulfilment of Berthelot's approximate "rule of maximum work."

7. A distinction is drawn between endothermic and pseudo-endothermic reactions.

8. If the change of total energy could be corrected for the heat energy displaced by change of heat capacity, a measure of the total affinities might be obtained, for into this heat the osmotic tendencies do not enter.

9. If the same contraction in volume as that exhibited on combining could be produced on the uncombined factors in the reaction by outside pressure under similar conditions, the work expended might serve as another measure of the total affinity.

10. In the absence of concentration-effect, the "attracting energy" of a given reaction probably lies between the change of free energy and the change of total energy.

11. It is shown that the hypothesis of compressible atoms affords a conceivable explanation of these facts, and that it is not inconsistent with either of the two laws of energy.

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